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DOI: https://doi.org/10.1016/j.commatsci.2019.01.040

Recent progress in computational exploration and design of functional materials

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Abstract

In this review, we summarize our work for the computational study and design of functional materials. Emphasis is laid on computational spectroscopy in the condensed phase as well as exploration of solar light-driven water splitting. In particular, dynamic *ab initio* methods have been in the focus of recent developments. This has enabled computationally efficient access to spectroscopic signatures, local properties, and innovative analysis of complex systems. Examples involve periodic subsystem density functional theory and density functional perturbation theory as well as (vibrational) spectroscopy such as Raman (optical activity) spectroscopy or sum frequency generation for in-depth study of interfaces. In addition, sophisticated approaches for exploration of water splitting processes are outlined, especially for water oxidation as one of the limiting factors for efficient water splitting devices. In-depth study of water oxidation mechanisms and related reaction networks in combination with (dynamic) consideration of environmental effects has allowed unprecedented new insight and discovery of essential factors influencing water oxidation behaviour, thus paving the way for novel design approaches for more efficient catalysts.
Keywords: computational catalysis, molecular dynamics, spectroscopy, in silico design, interface, water splitting, density functional theory

1. Introduction

Tailored materials are essential in today's world and a prerequisite to meet the upcoming future challenges in a wide range of areas. Their development and testing, however, is usually associated with a significant effort due to time- and cost-intensive synthesis and characterization of materials. An in-depth understanding of their structure, properties, and behaviour is thus highly desirable to pave the way for *informed* design of new materials with enhanced functionalities [1, 2, 3, 4, 5]. During the last decade(s),

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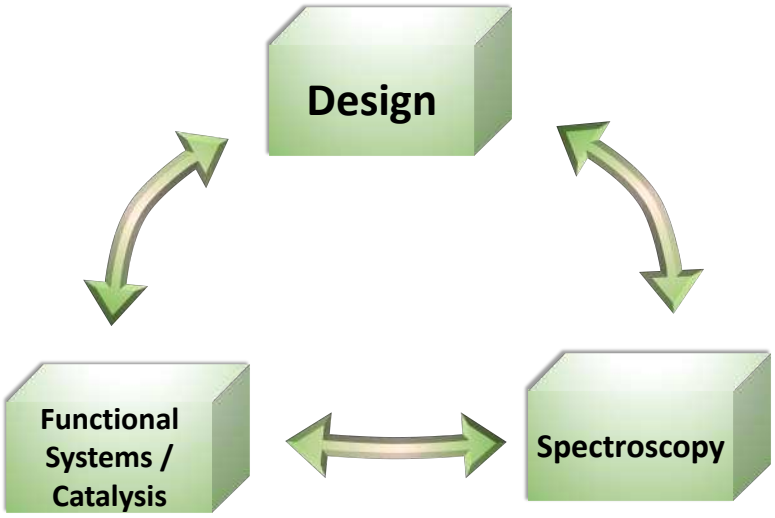
computational methods and infrastructures have greatly improved offering valuable complementary information to experimental data. Ideally, computational predictions are used at the first place before expensive, potentially hazardous experimental work is conducted. This has nowadays been utilized more and more in industry and academia. Worth mentioning along these lines are also various materials' initiatives which work on databases for comparison and screening of new materials using computational methods.

The natural link between experiment and simulation is spectroscopy, which gives indispensable information about the materials under study. Theoretical and computational spectroscopy have been an active field of research, and several developments in our group are outlined in this review. The focus of our work is on development and application of methods derived from quantum mechanics. Usually, density functional theory (DFT) is the workhorse for computational materials science due to the good compromise between accuracy and computational efficiency. Other methods used in our group are multireference wavefunction-based methods for (strongly) correlated materials, Quantum Monte Carlo, as well as hybrid quantum mechanics/molecular mechanics approaches. Besides that, emphasis has been put on *ab initio* (DFT-based) molecular dynamics (AIMD) in order to overcome limitations of static calculations. This has led to valuable novel insight for various compounds and processes. In this review, we limit ourselves to one of our directions for study of functional materials, namely solar light-driven water splitting. This is a promising, sustainable way to face the world's energy problem with continuously increasing energy demand and environmental problems such as global climate change. Using the information gained from investigation of water splitting processes provides highly useful information, which can be used to derive structure–activity relationships for *in silico* design (see Fig. 1). The latter lays the ground for informed development of more efficient, stable (catalytic) systems, in this way avoiding expensive approaches relying on, e.g., brute-force screening of materials.

This review is organized as follows: Our developments in the field of spectroscopy for the characterization of condensed phase systems are described in Section 2. Afterwards, our efforts for in-depth exploration and design of novel materials for solar light-driven water splitting are summarized in Section 3. Finally, a conclusion and outlook can be found in Section 4.

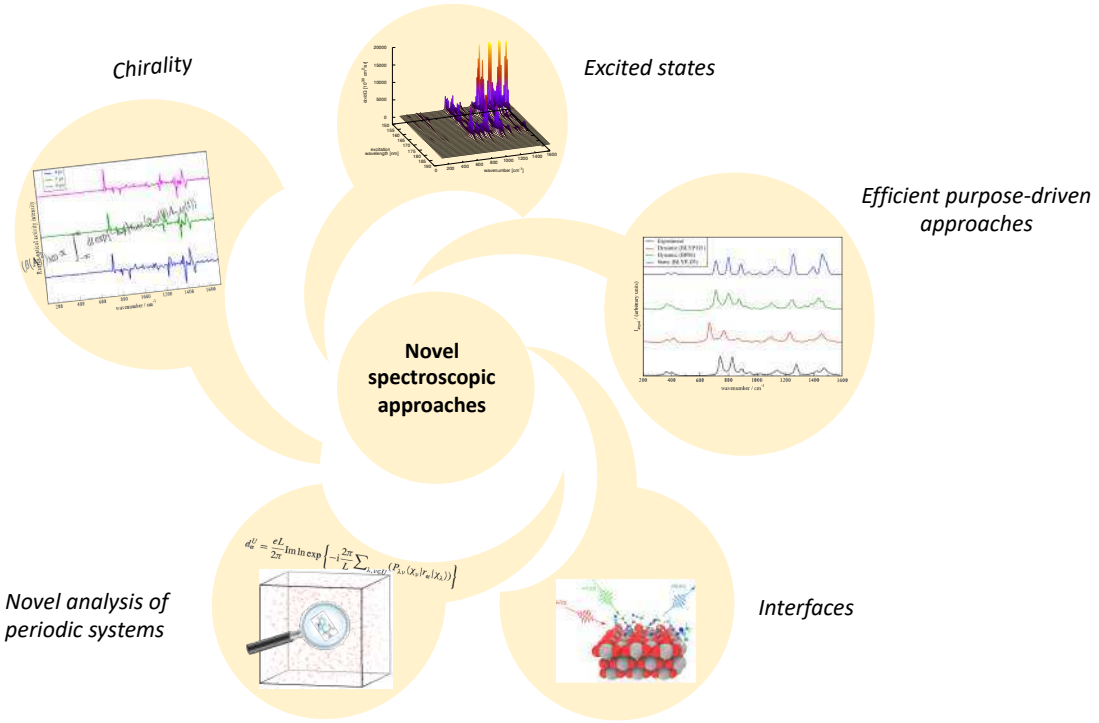
Figure 1: Research directions in our group described in this review: computational spectroscopy, exploration of functional compounds, and *in silico* design.



2. Recent developments for computational spectroscopy in the condensed phase

There is a large variety of spectroscopic methods, which can be applied depending on the question and material of interest. X-ray absorption spectroscopy, for instance, has been highly valuable for transition metal-containing systems and regularly used for the study of water splitting catalysts [6, 7, 8]. In this context, refinement procedures for an improved agreement of experimental spectroscopic data and computational models have been developed as well [9, 10]. Going to the less energetic UV/Vis region, corresponding absorption spectra are routinely measured in laboratories. One of our recent efforts in this field has focused on real time propagation as a method to obtain excited state information and related spectra [11]. This approach offers a more attractive scaling for large systems compared to common perturbation theory-based methods, and a whole spectrum can be computed with only one run. Besides that, vibrational spectroscopy is essential and various developments are highlighted in more detail in the following [12] (see Fig. 2).

Figure 2: Examples for our research in the field of spectroscopy: First Raman optical activity spectrum from AIMD (top, left-hand side; adapted from Ref. [13]), first excitation profile for (Resonance) Raman spectroscopy obtained with real time propagation (top, middle; adapted from Ref. [11]), novel analysis of periodic systems (bottom, left-hand side; see Ref. [14] for further details), purpose-driven approaches for AIMD (middle, right-hand side; adapted from Ref. [15]), and sum frequency generation spectroscopy for study of interfaces (bottom, right-hand side; adapted from Ref. [16]).



2.1. Periodic subsystem density functional theory and IR spectroscopy

A very common type is Infrared (IR) spectroscopy the calculation of which requires the changes of the electric dipole moment due to vibrational motion. Electric dipole moments for nonperiodic systems can be calculated in a straightforward manner. Within Kohn–Sham (KS) DFT and the Gaussian and plane waves (GPW) [17, 18] method, the electronic part can be calculated in the usual way as [14]

$$d_\alpha^{\text{nonper}} = -e \sum_i f_{occ} \langle \psi_i | r_\alpha | \psi_i \rangle = -e \sum_{\mu,\nu} (P_{\nu\mu} \langle \chi_\mu | r_\alpha | \chi_\nu \rangle) \tag{1}$$

with the density matrix $P_{\nu\mu}$ and atomic basis functions $\{|\chi_\nu\rangle\}$. $\{|\psi_i\rangle\}$ are the KS orbitals, r_α the position operator for the electron in α Cartesian direction, and e the elementary charge. We assume the same occupation number f_{occ} for all KS orbitals. Yet, for a sophisticated description of liquids, surfaces, and

solid state systems, periodic boundary conditions are usually applied. This leads to an ill-defined position operator in Eq. (1). In order to circumvent this issue, the velocity representation for the position operator can be employed. Alternatively, the Berry phase formula for electric polarization is regularly used for insulators [19, 20], which is given for a cubic simulation cell with side length L (and considering the Γ point of the Brillouin zone only) as

$$d_\alpha = f_{\mathrm{occ}} \frac{eL}{2\pi} \mathrm{Im} \ln \det \boldsymbol{S}_\alpha \tag{2}$$

with the matrix elements (m, n correspond to occupied KS orbitals)

$$S_{\alpha,mn} = \left\langle \psi_m \left| \exp\left\{ -\mathrm{i} \frac{2\pi}{L} r_\alpha \right\} \right| \psi_n \right\rangle . \tag{3}$$

If further insight into the origin of the bands in IR spectra and deeper analysis of the material under study are required, it is highly desirable to calculate local properties such as electric dipole moments of only parts of the whole system. This is standardly done by localization of KS orbitals leading to maximally localized Wannier functions (MLWFs) [21]):

$$|\tilde{\psi}_l\rangle = \sum_i U_{li} |\psi_i\rangle. \tag{4}$$

The electronic part of the electric dipole moment for a subsystem W is then calculated as

$$d_\alpha^{W,\mathrm{WC}} = -e f_{\mathrm{occ}} \sum_{t \in W} r_{\alpha,t}^{\mathrm{WC}} = -e f_{\mathrm{occ}} \sum_{t \in W} \left(-\frac{L}{2\pi} \mathrm{Im} \ln s_{\alpha,t} \right) \tag{5}$$

with

$$s_{\alpha,t} = \left\langle \tilde{\psi}_t \left| \exp\left\{ -\mathrm{i} \frac{2\pi}{L} r_\alpha \right\} \right| \tilde{\psi}_t \right\rangle . \tag{6}$$

where $\boldsymbol{r}_t^{\mathrm{WC}}$ are Wannier centers.

We have recently suggested another route to local properties [14]. Our approach is based on subsystem DFT where the whole system is treated with Hohenberg–Kohn (HK) DFT and subsystems with the more accurate KS DFT, leading in total to a computational speed-up. The first implementation of periodic subsystem DFT has been available in the CP2K package [22], which has been recently extended to hybrid density functionals [14]. As has been derived in Ref. [14], the α component of the electronic part of the electric dipole moment for subsystem W can be obtained as

$$d_\alpha^W = \frac{eL}{2\pi} \mathrm{Im} \ln \exp\left\{ -\mathrm{i} \frac{2\pi}{L} \sum\nolimits_{\lambda,\mu \in W} \left(P_{\lambda\mu} \langle \chi_\mu | r_\alpha | \chi_\lambda \rangle \right) \right\}, \tag{7}$$

which has been used to compute e.g. first IR spectra from periodic subsystem DFT [14].

Eq. (7) has several advantages: No MLWFs are needed, the localization of which can be computationally demanding; Eq. (7) can be used in linear-scaling DFT, and it is exact within the derivation using subsystem DFT approach as described in Ref. [14] whereas using MLWFs potentially suffers from inaccuracies due to the localization procedure. In addition, it is not necessary to assign electrons to atoms as for MLWFs. A general limitation of DFT embedding schemes is the approximation used for the kinetic energy density functional, which can reduce the accuracy depending on the system under study.

2.2. Ab initio molecular dynamics for vibrational spectroscopy

Another direction in our research has been the development of AIMD-based methods for spectroscopy, in particular vibrational spectroscopy. Standard computational approaches rely on static calculations treating the system at its equilibrium structure and a temperature of 0 K (and mostly employing the harmonic approximation). In contrast to that, AIMD allows calculations at varying thermodynamic conditions such as different temperatures and pressures, providing thus a more realistic description and possibly closer to experimental conditions. Moreover, sampling of the conformational phase space, hydrogen-bonding dynamics, and other local geometric arrangements is obtained. Environmental effects can therefore be included in a sophisticated way. The AIMD approaches described in this review rely on Born–Oppenheimer molecular dynamics. The nuclei are treated as classical particles and move according to Newton's equation of motion in a potential given by the Born–Oppenheimer potential energy surface, which is derived by solving the electronic Schrödinger equation and corresponding electronic energy gradients at each nuclear configuration [23]. This usually comes with a significant increase in computational effort compared to the static approach. An additional advantage of the AIMD approach for vibrational spectroscopy is the inclusion of certain anharmonicities since no assumption about the potential energy surface is made, which surpasses static approaches relying on the harmonic approximation. Moreover, band shapes can be directly obtained from the calculation whereas an artificial broadening has to be applied in static approaches.

2.3. Raman spectroscopy and variants thereof

Apart from IR measurements, Raman spectroscopy is another important, regularly applied technique. Evaluation of electric-dipole–electric-dipole polarizabilities is needed for the computation of Raman spectra. The latter can be derived from the above mentioned velocity form of the position operator or the Berry phase formulation. We have implemented the calculation of Raman spectra for periodic systems within the GPW scheme using efficient density functional perturbation theory [24, 15]. This scheme

is superior to previous approaches relying on numerical derivatives using applied external fields [25], which are in general less accurate and computationally more demanding. An efficient scheme for local polarizabilities has been presented as well, which does not require computationally expensive localization procedures [15]. This implementation has been extended to Raman optical activity, the chiral variant of Raman spectroscopy. The latter provides valuable information about chiral systems, and the very first entirely AIMD-based spectra have been presented recently [13]. Moreover, novel analysis and calculations of Raman optical activity using localized molecular orbitals has been developed, being an important step towards its extension to periodic systems [26]. Other studies concerned the influence of environmental effects [27, 28, 29]. The first review dealing with Raman optical activity for coordination compounds [30, 31] and the rather unexplored area of solids as well as other variants like magnetic Raman optical activity can be found in Ref. [32].

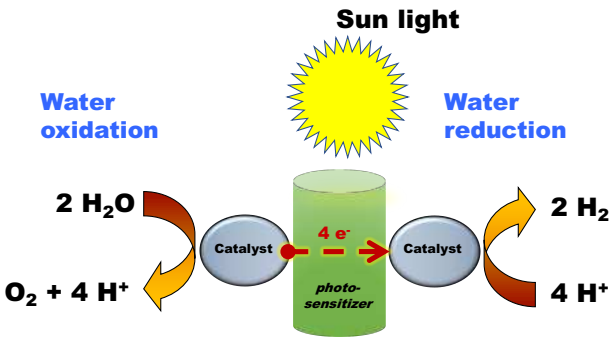
2.4. Sum frequency generation for elucidation of interfaces

Ubiquitous in chemistry and materials science are interfaces such as gas–liquid, liquid–liquid, gas–solid or liquid–solid interfaces. In order to gain deeper knowledge about the structure and dynamics at the interface, vibrational spectroscopy can be applied. In particular sum frequency generation (SFG) spectroscopy has become more and more popular in recent years. It relies on a second-order nonlinear process where two laser beams are used, one in the visible range, and one in the IR range. This allows to deduce orientation and structural composition of e.g. molecules at the interface. In contrast to classical molecular dynamic or static DFT-based calculations, simulations based on AIMD have been rarely applied for the modelling of SFG spectra, mostly for liquids (see, e.g. Refs. [33, 34, 35, 36, 37]). We have used an approach using density functional perturbation theory, which has allowed to obtain a pioneering SFG spectrum for a computationally quite expensive semiconductor surface [16]. We have chosen TiO_2 due to its favorable properties, especially as functional material for energy storage and conversion. The surface studied in Ref. [16] is a rutile (110) surface with acetonitrile gas molecules adsorbed. Corresponding experimental measurements have been presented in Ref. [38]. The orientations of the molecules obtained from the AIMD calculations [16] are on average in good agreement with orientational parameters derived from experimental data and empirical modelling [38]. This has opened exciting new ways for detailed study of insulator/semiconductor-involving interfaces. Moreover, this AIMD approach offers, as mentioned in Section 2.2, several advantages compared to static calculations such as consideration of the dynamics at ambient conditions and inclusion of certain anharmonicities as well as band shapes in the spectra without the necessity of artificial broadening.

3. Artificial water splitting for clean and renewable energy

Spectroscopy is an indispensable tool for detailed investigation of a large variety of compounds. This is also true for the study and design of functional materials where we have especially focused on photocatalysis. We have dealt with solar light-driven water splitting as a promising solution to the world's increasing energy demand, in particular in view of global climate change and expected shortage of fossil fuels, with the sun as powerful, sustainable energy source. Water splitting consists of two half reactions: On the one side, there is water oxidation which generates molecular oxygen, protons, and electrons from water by means of a water oxidation catalyst (WOC); On the other side, water reduction takes place which produces molecular hydrogen with the help of an appropriate catalyst (see Fig. 3). Despite of huge research efforts, the development of stable and efficient water splitting devices is still highly sought-after. From the computational side, modelling of these processes has also been a hot topic of research with various open challenges (for reviews, see, e.g., Refs. [39, 40, 41, 42, 43, 44]). Currently, one of the main limiting factors is the water oxidation for which stable and active catalysts are desirable. In addition, structure–activity relationships are very helpful for informed development of novel WOCs.

Figure 3: Scheme of a solar light-driven water splitting device.



3.1. Methodological aspects

A prerequisite for smart design of more efficient WOCs is the understanding of the entire water oxidation process. The catalyst and its water oxidation behaviour have thus to be elucidated thoroughly. This

includes the detailed structure of the catalyst as well as the mechanism of water oxidation and related reaction networks such as side, deactivation, and decomposition pathways. We have shown that environmental effects can have a decisive influence on the structure and reactivity of the catalyst. This has, for instance, been elucidated for the generation of the active species for water oxidation (catalytic ground state), which has significantly been affected by the solvent environment [7, 45, 46]. The solvent environment can be included into the calculations in several ways: A solvent continuum model can be used, which mimics "average" solvent effects (fitted for certain test set and thermodynamic conditions) but has shortcomings, e.g., for description of directed bonds such as hydrogen bonds. In order to ameliorate the latter, explicit solvent molecules may be included into the model, possibly in combination with a solvent continuum model. Subsequent optimization of the model can lead to an improved description of the system but the outcome of the optimization is dependent on the initial guess for the optimization process and may thus not adequately represent the system. In contrast to that, the computationally more expensive AIMD approach allows exploration of the conformational phase space at ambient conditions, thus naturally accounting for aspects like hydrogen-bonding networks and conformational dynamics. This is especially important since water is essential for water oxidation, and its dynamics, associated proton transfers, and hydrogen bonding networks play a vital role. Other ingredients in the reaction mixture, which are usually neglected in the simulations, may also directly interact with the catalyst as shown for possible inhibitory effects of buffer molecules [7].

After determination of the catalytic ground state, the next step is the elucidation of the water oxidation mechanism. Free energies can be computed for each state during the catalytic cycle, providing a thermodynamic description of this process. Computation of the barriers connecting the different states gives information about the kinetics of the process. This knowledge can further be employed for microkinetic modelling in order to enable a comparison of experimental and calculated turnover frequencies and turnover numbers. Emphasis has been put on AIMD-based approaches, which have been quite rarely used in this field but provide several distinct advantages. Going beyond the static picture, free energies and barriers can be obtained with AIMD using e.g. enhanced sampling methods such as metadynamics [47, 45], which gives access to entire free energy surfaces (compare Fig. 5). Aside from that, the energetics of proton coupled electron transfer frequently occurring in water oxidation catalysis has been elucidated using a thermodynamic integration-based AIMD protocol [48], which can also be applied to prediction of properties such as redox potentials [49]. Since DFT has difficulties to describe the involved electronic structure of (strongly coupled) transition metals in an highly accurate way as required for, e.g., spin state energetics important for water oxidation catalysis, multiconfigurational wavefunction-based

approaches have been explored for the description of WOCs as well [50]. Standard approaches such as complete active space self consistent field (CASSCF) methods are, however, limited to rather small systems. CASSCF Quantum Monte Carlo [51] offers a promising way for larger systems and is currently investigated for exploration of larger systems than feasible with conventional approaches.

3.2. Study and design of water splitting catalysts

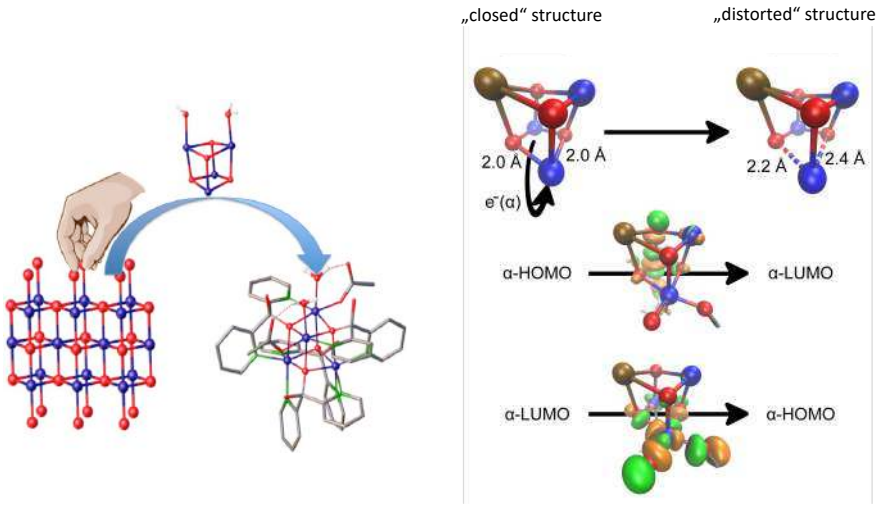
WOCs featuring a cubane core are attractive catalysts due to their similarity with nature's highly efficient oxygen evolving complex (OEC). The latter features a cubane core with three redox-active Manganese metal centers and a redox inert Calcium metal center connected via oxo bridges in addition to a fourth "dangling" Manganese center. Artificial Mn/Ca-based cubanes closely mimicking nature's oxygen-evolving complex, however, have not been found to be particularly active for artificial water oxidation, and Co-based cubanes for water oxidation have attracted attention as well (for a review, see Ref. [52]). The latter are also building blocks for heterogeneous catalysts such as the Co-based amorphous catalyst in the "artificial leaf" by Nocera and co-workers [53, 54, 55], which shows attractive self-healing and self-assembling properties. In close collaboration with experimental groups, we have presented the first Co(II)-based cubane WOCs, which are some of the rare stable and active cubane WOCs presented up to now [6, 7, 8]. The latest generation of these Co(II)-WOCs is shown in Fig. 4. This catalyst has two aqua ligands at the same face of the cage, thus mimicking a surface of a heterogeneous Cobalt-oxide WOC [8]. AIMD simulations have shown that the structure of the cubane cage is flexible but no decomposition of this catalyst has been observed in the calculations in agreement with experimental data. Furthermore, a highly dynamic hydrogen bonding network and various proton transfers have been observed in the AIMD trajectories, which demonstrates how easily this WOC can change its protonation state [8].

The first Co(II)-cubane WOCs $\{Co_4(OR)_4\}$ (R = hmp) were published in 2013 [6] followed by Lanthanide (Ln)-containing cubane WOCs $\{Co_3Ln(OR)_4\}$ [7] (Ln = Er, Tm, Yb, Ho) in 2015. The latter surpass the first generation in terms of catalytic activity whereby the cubane with the redox-inert Erbium cation is the most active catalyst in the series of the $\{Co_3Ln(OR)_4\}$ WOCs. This reminds of nature's OEC which also includes a redox-inert metal cation.

After detailed elucidation of the catalytic ground state [6, 7, 45], possible water oxidation mechanisms have been examined [56, 57, 58]. Emphasis has been put on two commonly known mechanisms, nucleophilic water attack and oxo–oxo coupling (and modifications thereof). Selected barriers were explored using e.g. nudged elastic band calculations. Inclusion of explicit solvent molecules turned out to be crucial in order to capture certain effects such as alleviation of the nucleophilic water attack due to proton abstraction of

a basic site closeby. In addition, spin states have been found to have a pivotal function as has the entire cubane cage during catalysis. Comparing the $\{Co_4(OR)_4\}$ WOC to the $\{Co_3Ln(OR)_4\}$ WOCs, various differences have been detected. The $\{Co_3Ln(OR)_4\}$ (Ln=Er, Tm) WOCs show an astonishing structural flexibility due to exchange reactions with water molecules, facile change of protonation and oxidation state, and even of the cubane core going along with change in coordination environment. In the dynamic calculations, several cubane cages have been observed ranging from a "closed" cubane cage as found in the X-ray structure over "distorted" [57] (see Fig. 4) to "open" cubane structures [58]. This is reminiscent of open cubane structures and redox isomerism found in nature [59] and presents such a first case for artificial WOCs. Our observations suggest that the distinct properties of the $\{Co_3Ln(OR)_4\}$ (Ln=Er, Tm) catalysts and their interplay form the basis for the measured higher catalytic activity compared to the $\{Co_4(OR)_4\}$ WOC.

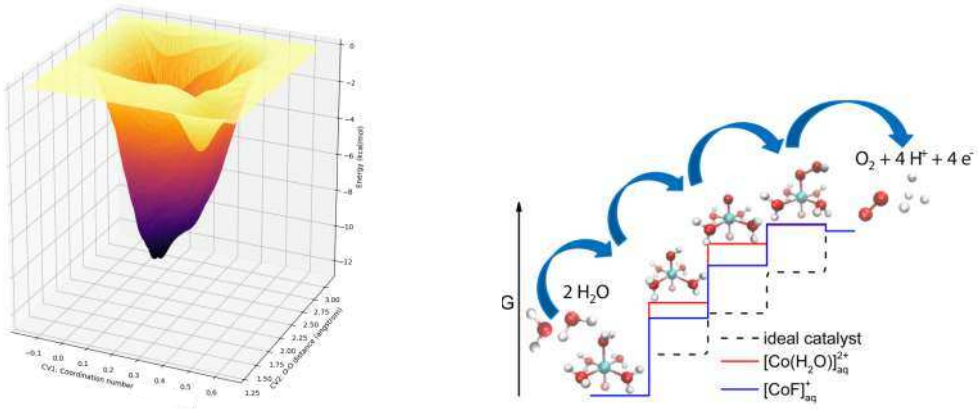
Figure 4: Right-hand side: Co(II)-based cubanes as surface mimics of a Cobalt-oxide catalyst (reprinted with permission from J. Am. Chem. Soc. 139 (2017) 14198; Copyright 2017 American Chemical Society); Left-hand side: "closed" and "distorted" cubane structures of the $\{Co_3Tm(OR)_4\}$ cubane and associated change in frontier orbitals [57] (reproduced with permission from ACS Catalysis 6 (2016) 6750; 2016 American Chemical Society).



The obtained information about the behaviour of the catalysts forms an essential basis for derivation of design guidelines for new catalysts in this field. As mentioned above, an important aspect is the flexibility with respect to spin states, oxidation and protonation states as well as nuclear structure. Another major point has been the observation that the catalysis does not only affect the metal center attached to the species which is changed during the water oxidation cycle and oxidized to O_2 but also neighbouring

metal centers. The crucial influence of the latter can be seen, e.g., in frontier orbitals and spin densities. Moreover, we suggested certain changes in the ligand environment to make the exchange with water from the solvent environment more flexible [56, 7]. There is also the possibility to lower the barrier for rate-limiting steps such as the nucleophilic water attack by modification of the ligand environment, in this way tuning certain frontier orbitals [56, 57, 60] for faster kinetics of this process. A commonly applied concept in heterogeneous catalysis is the concept of a thermodynamically ideal catalyst, which has the free energy required for water oxidation equally shared between the steps in the catalytic cycle, thus leading to minimum overpotential during the catalytic cycle (compare Fig. 5) [56, 57, 61, 58, 60]. We have adapted this concept for the cubane WOCs and could thus derive steps in the catalytic cycle which deviate significantly from such a behaviour and might be improved. This provides a tool for first assessment of the thermodynamic behaviour of WOCs during *in silico* design of novel WOCs. Beyond that, selected frontier orbitals can serve as a first indicator for a lowering or increase of barriers of certain steps [56, 57, 61, 58] during the design process.

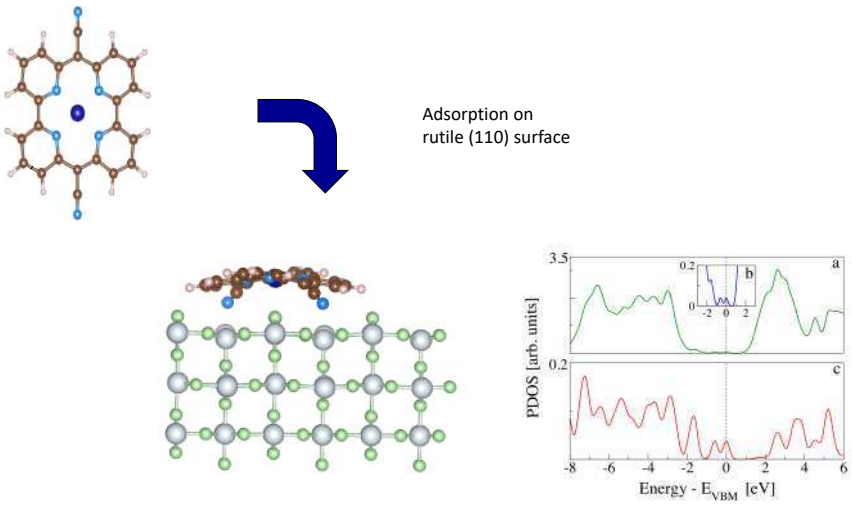
Figure 5: Example of a free energy surface for a nucleophilic water attack at a Ru-based WOC obtained with metadynamics (left-hand side) and design of model WOCs by comparison to a thermodynamically ideal catalyst (right-hand side) (adapted from Ref. [61]).



Besides Co-based WOCs, Ru catalysts have been explored in detail in collaboration with experimental groups [62, 46]. Possible descriptors for efficient *in silico* design have been explored in Ref. [60], and systematic *in silico* design has led to vital insight and a novel improved catalyst [60]. Other work has, for instance, dealt with adsorption of a water reduction catalyst on a functional surface [63] (see Fig. 6).

This is an essential step for elucidation of the interaction between the molecular catalyst and the surface and associated changes in nuclear and electronic properties, which can lead to a significant alteration of catalytic behaviour.

Figure 6: Adsorption of a water reduction catalyst (left-hand side) on rutile (110) surface (middle) and corresponding density of states (right-hand side) (for details, see Ref. [63]; adapted from Ref. [63] with permission from the PCCP Owner Societies).



4. Conclusion and outlook

We have briefly reviewed our recent work on exploration and design of materials. Emphasis has been put on new approaches for spectroscopy and catalysis in the condensed phase. Innovative strategies such as periodic DFT embedding have been developed for computationally cheap access to analysis of complex systems and local properties of systems obeying periodic boundary conditions. Moreover, novel methods based on forefront high-performance AIMD have been derived, which takes into account the dynamics of systems and can explore them at ambient conditions in contrast to common static approaches. This is especially vital for materials with high structural flexibility and sophisticated inclusion of solvent and environmental effects such as hydrogen-bonding networks.

It has been shown that this approach leads to very good agreement with experiment, in particular for vibrational spectra for which it considers anharmonicities and provides realistic band shapes. Methods described range from efficient computation and detailed analysis of vibrational spectra such as IR and

Raman spectra to surface- and chirality-sensitive approaches. For instance, efficient access to response properties as needed, e.g., in Raman (optical activity) spectroscopy has been presented using density functional perturbation theory in combination with creative local analysis of contributions. In addition, the first fully AIMD-based spectrum in the field of Raman optical activity spectroscopy has been described. Structure and dynamics at interfaces can be elucidated using sum frequency generation spectroscopy, for which an efficient AIMD approach allowed the first such study for a semiconductor surface. These approaches have enabled fascinating new possibilities for accurate investigation and novel insight into the behaviour of materials.

Spectroscopy is very valuable to link calculations to experiment and indispensable for study of functional materials. A strong direction in our group has been solar light-driven water splitting as a promising way for sustainable energy storage and conversion. In collaboration with experimental groups, we have worked on Co-based cubane catalysts, which are attractive mimics for nature's efficient oxygen evolving complex and possible building blocks for heterogeneous catalysts such as self-healing Cobalt oxide-based water oxidation catalysts. It has been demonstrated that environmental and solvent effects play a decisive role. We have therefore focused on AIMD techniques for investigation of water oxidation catalysis, in particular calculation of free energies and barriers, reaction networks, and relevant properties. For electronic structure beyond DFT, more accurate wavefunction-based approaches have been explored as well. This thorough approach made clear that the various catalysts show a different behaviour, which can also be correlated with varying catalytic activity observed in experiment. An astonishing flexibility of the cubane cage has been observed in several cases going along with complex interaction with water from the environment and facile proton transfers. In this context, distinct types of cubane structures have been observed for Ln-containing cubanes including a so-called open cubane structure reminiscent of findings for nature's oxygen evolving complex. Other attractive features include flexible change in oxidation and protonation states, coordination environment and lowering of barriers due to a basic site closeby. Moreover, important knowledge about the thermodynamics and kinetics of the water oxidation mechanisms has been obtained, which has further been used to assess their performance using creative approaches and to obtain innovative design guidelines for novel efficient catalysts. This has been complemented by informed *in silico* design of Ru-based water oxidation catalysts as well as in-depth elucidation of the behaviour of molecular catalyst on a functional surface.

The described topics in combination with forefront *ab initio* methods clearly show that modelling is an indispensable tool in today's materials science, whose impact is expected to increase even further in the future thanks to more efficient and/or accurate computational approaches and growing computer

power, possibly in combination with methods from artificial intelligence. This opens exciting new ways for computational exploration and design of a broad variety of functional materials.

Acknowledgment

Funding by the University of Zurich, the Swiss National Science Foundation (grant no: PP00P2_170667), and the University Research Priority Program LightChEC is gratefully acknowledged. The author thanks the Swiss National Supercomputing Center for computing resources (project ID: s502, s745, and s788) and all current and previous group members who contributed to the work described in this manuscript. Their names can be found in the corresponding references.

Data availability

Since this manuscript is a review mostly describing previously published work, the raw/processed data required to reproduce these findings cannot be shared at this time.

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